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ENT-KAURENE DITERPENOIDS FROM *RABDOSIA LEUCOPHYLLA*

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Key Word Index—*Rabdosia leucophylla*; Labiatae; *ent*-kaurenoid; leucophyllin A–D.

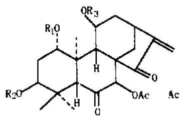
Abstract—Four new *ent*-kaurenoids, leucophyllin A–D, were isolated from the aerial part of *Rabdosia leucophylla*. Their structures were elucidated on the basis of spectroscopic and chemical evidence as *ent*-1β-hydroxy-3α,7α,11α-triacetoxykaur-16-en-6,15-dione, *ent*-1β,11α-dihydroxy-3α,7α-diacetoxykaur-16-en-6,15-dione, *ent*-1β,11α,15α-trihydroxy-3α,7α-diacetoxykaur-16-en-6-one and *ent*-6β,11α-dihydroxy-1β,3α,7α-triacetoxykaur-16-en-15-one. The structure of leucophyllin C was also confirmed by X-ray crystallographic analysis. © 1997 Elsevier Science Ltd

INTRODUCTION

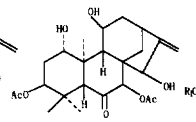
The genus *Rabdosia* is rich in diterpenes, especially highly oxidized *ent*-kaurene diterpenoids with biological activity [1, 2]. *Rabdosia leucophylla* (Dunn) Hara is distributed mainly over western Sichuan and the north-western Yunnan provinces in China. This paper describes the isolation and structural elucidation of four new *ent*-kaurene diterpenoids, leucophyllin A(**1**), B(**2**), C(**3**) and D(**4**), from the aerial parts of the plant.

RESULTS AND DISCUSSION

Leucophyllin A (**1**), $C_{26}H_{34}O_9$ (HRMS), was obtained as colourless needles. It has a five membered ring with a ketone group conjugated with an exomethylene group, as shown by following spectral data: UV λ_{max} ($CHCl_3$) (log ε): 242 nm (5.41); IR ν_{max}^{KBr} cm^{-1}: 1716 and 1648; ^{1}H NMR: δ 5.90 and 5.18 (each 1H, *br s*); ^{13}C NMR: δ 210.8, 149.7 and 113.0. It also contains three tertiary methyl groups [δ_H 1.40, 1.31 and 0.89 (each 3H, *s*); δ_C 25.6, 21.4 and 14.1], an isolated ketone group (δ_C 205.8), a hydroxyl group [IR ν_{max}^{KBr} cm^{-1}: 3438; δ_H 5.80 (1H, *br s*, disappeared after D_2O treatment); δ_C 75.1], three acetoxyl groups [δ_H 2.23, 2.01 and 1.72 (each 3H, *s*); δ_C 169.6, 169.6 and 169.2] and four methine protons on a carbon having a functional oxygen group [δ_H 4.45 (1H, *dd*, J = 5, 11 Hz), 4.78 (1H, *t*, J = 5 Hz), 5.16 (1H, *s*) and 6.67 (1H, *d*, J = 3 Hz); δ_C 75.1, 77.5, 80.1 and 69.8]. The ^{13}C NMR spectrum shows, in addition to the signals mentioned above, the presence of three methylene groups, three methine groups and three quaternary carbon atoms. In view of the structures of related diterpenoids isolated from the genus *Rabdosia* [3], **1** has a structure in which a ketone, a hydroxyl and three acetoxyl groups are substituents of the *ent*-kaur-16-en-15-one skeleton.



	R1	R2	R3
1	H	Ac	Ac
2	H	Ac	H
5	Ac	H	Ac
6	Ac	Ac	Ac



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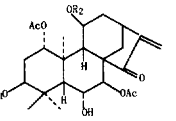

	R1	R2
4	Ac	H
7	H	Ac
8	Ac	Ac

The ^{13}C NMR spectral data of **1** are very similar to those of adenanthin (**5**) [4], while its ^{1}H NMR spectrum contains important differences from that of **5**, indicating that **1** has the same structural pattern as **5** except for the substituents on C-1 and C-3. The downfield shift of H-3 (δ 4.78) and the upfield shift of H-1 (δ 4.45) of **1** compared with those of **5** can be attributed to the transposition of the oxygen functional groups at C-1 and C-3 of **5**, in which case, the signals for H-3 and H-1 are at δ 4.28 and 5.99, respectively. Acetylation of **1** and **5** with acetic anhydride in pyridine in the usual manner gives the same derivative (**6**). The ^{13}C NMR spectrum of **6** indicates that there are no hydroxyl groups but an extra acetoxyl group (δ_C 170.0, 78.3) compared with **1**. In the ^{1}H NMR spectrum, the signal due to H-1 is shifted downfield from δ 4.45 in **1** to δ 5.21 in **6**. These facts support the assumption that a hydroxyl group is located at the C-1 position. Thus, the structure of leucophyllin A(**1**) is that of *ent*-1β-hydroxy-3α,7α,11α-triacetoxykaur-16-en-6,15-dione.

Leucophyllin B (**2**), $C_{24}H_{32}O_8$ (HRMS), was isolated

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Table 1. ^{13}C NMR data for diterpenoids **1**–**5** and **7** (in pyridine-d_5)

C	1	2	3	4	5	7
1	75.1(*d*)*	73.6(*d*)	75.1(*d*)	80.8(*d*)	79.4(*d*)	81.0(*d*)
2	32.4(*t*)	31.8(*t*)	32.8(*t*)	29.4(*t*)	32.8(*t*)	33.4(*t*)
3	77.5(*d*)	77.6(*d*)	78.2(*d*)	79.0(*d*)	74.9(*d*)	76.2(*d*)
4	35.0(*s*)	36.3(*s*)	35.7(*s*)	37.3(*s*)	36.9(*s*)	38.8(*s*)
5	51.7(*d*)	55.8(*d*)	53.5(*d*)	43.0(*d*)	51.3(*d*)	41.6(*d*)
6	205.8(*s*)	205.0(*s*)	207.3(*s*)	68.9(*d*)	206.6(*s*)	70.3(*d*)
7	80.1(*d*)	78.3(*d*)	79.1(*d*)	75.7(*d*)	80.9(*d*)	75.8(*d*)
8	52.9(*s*)	52.0(*s*)	50.8(*s*)	48.7(*s*)	53.3(*s*)	49.1(*s*)
9	55.1(*d*)	60.0(*d*)	53.1(*d*)	59.2(*d*)	55.2(*d*)	55.5(*d*)
10	50.2(*s*)	47.5(*s*)	48.2(*s*)	43.1(*s*)	49.8(*s*)	43.5(*s*)
11	69.8(*d*)	64.5(*d*)	64.6(*d*)	66.6(*d*)	68.9(*d*)	69.3(*d*)
12	36.8(*t*)	40.2(*t*)	42.6(*t*)	41.4(*d*)	38.2(*t*)	38.6(*t*)
13	35.6(*d*)	35.7(*d*)	37.9(*d*)	37.7(*d*)	36.2(*d*)	37.0(*d*)
14	33.1(*t*)	32.1(*t*)	33.0(*t*)	37.3(*t*)	34.0(*t*)	37.0(*t*)
15	201.8(*s*)	203.0(*s*)	83.8(*d*)	205.9(*s*)	201.6(*s*)	205.6(*s*)
16	149.7(*s*)	151.3(*s*)	158.6(*s*)	151.7(*s*)	150.4(*s*)	151.1(*s*)
17	113.0(*t*)	113.1(*t*)	106.1(*t*)	110.3(*t*)	113.6(*t*)	113.1(*t*)
18	25.6(*q*)	27.0(*q*)	26.5(*q*)	28.1(*q*)	27.2(*q*)	29.6(*q*)
19	21.4(*q*)	21.4(*q*)	21.7(*q*)	23.9(*q*)	22.7(*q*)	24.7(*q*)
20	14.1(*q*)	14.5(*q*)	14.2(*q*)	15.8(*q*)	15.5(*q*)	16.1(*q*)
$CH_3\underline{C}O$	169.6(*s*)	169.5(*s*)	169.8(*s*)	170.1(*s*)	170.1(*s*)	170.2(*s*)
	169.6(*s*)	169.4(*s*)	169.5(*s*)	170.1(*s*)	169.8(*s*)	170.2(*s*)
	169.2(*s*)			169.3(*s*)	169.1(*s*)	169.3(*s*)
$\underline{C}H_3CO$	20.6(*q*)	20.2(*q*)	20.3(*q*)	21.4(*q*)	21.7(*q*)	21.9(*q*)
	20.2(*q*)	20.1(*q*)	20.2(*q*)	21.3(*q*)	20.9(*q*)	21.3(*q*)
	20.1(*q*)			20.7(*q*)	20.8(*q*)	21.3(*q*)

* Multiplicities of signals were determined by DEPT techniques.

as colourless needles. It has similar NMR spectral data to those of **1**. However, **2** has only two acetoxyl groups [δ_H 2.20, 1.96 (each 3H, *s*); δ_C 77.6, 78.3, 169.5 and 169.4]. The difference between **1** and **2** is the upfield shift of C-11 from δ 69.8 in **1** to δ 64.5 in **2**, the downfield shift of C-9 and C-12 from δ 55.1 and 36.8 to δ 60.0 and 40.2, respectively. These facts, together with the same coupling constants of H-11 of **2** and **1** indicate that there is a hydroxyl group instead of an acetoxyl group at the 11β-position. Acetylation of **2** with acetic anhydride in pyridine in the usual manner affords a diacetate which is identical to **6** by ^1H NMR and ^{13}C NMR. The hydroxyl groups at C-1 and C-11 in **2** are acetylated as shown by the downfield shift of δ_H (in $CDCl_3$): 3.96 and 4.38 to 5.52 and 5.56, respectively. Accordingly, the structure of **2** is *ent*-1β,11α-dihydroxy-3α,7α-diacetoxykaur-16-en-6,15-dione.

Leucophyllin C (**3**), $C_{24}H_{34}O_8$ (HRMS), was obtained as colourless needles. Its ^{13}C NMR spectrum is similar to that of **1** especially for ring A (Table 1). It has an exo-methylene group on a five membered ring [δ_H 5.37 and 5.16 (each 1H, *br s*); δ_C 158.6 and 106.1], an isolated ketone group (δ 207.3), and three secondary hydroxyl groups and two secondary acetoxyl groups based on the following data: δ_H 4.56 (1H, *dd*, $J = 5$, 11 Hz) 4.85 (1H, *t*, $J = 3$ Hz), 5.25 (1H, *s*), 5.64 (1H, *m*) and 4.62 (1H, *m*), 2.24 and 1.95 (each 3H, *s*); δ_C 75.1, 78.2, 79.1, 64.6 and 83.8, 169.8 and 169.5. According to the ^{13}C NMR data of reported *ent*-kaurenoids [5], the chemical shift of C-13 (δ 37.9) indicates that there are no oxygen substituents on C-12 and C-14; the chemical shifts of C-9 and C-8 (δ 53.1 and 50.8) suggest that two oxygen substituents are at the 11-β and 15-β positions; the chemical shifts of C-16 (δ 158.6) and C-17 (δ 106.1) suggest that there is a hydroxyl group at the 15-β position; the chemical shifts of C-11 and C-12 (δ 64.6 and 42.6) indicate that the substituent at the 11β- position is a hydroxyl group. Accordingly, **3** is *ent*-1β,11α,15α-trihydroxy-3α,7α-diacetoxykaur-16-en-6-one. The structure was unambiguously confirmed by X-ray analysis. A perspective view of the molecule is shown in Fig. 1.

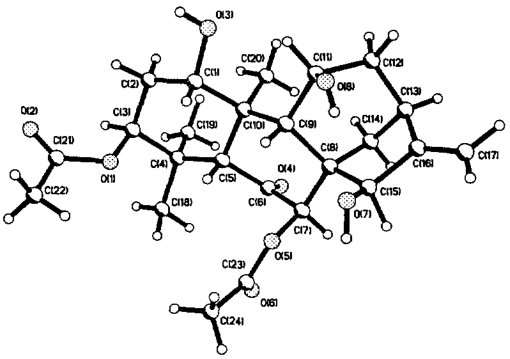

Fig 1. Perspective view of **3**.

Leucophyllin D (**4**), $C_{26}H_{36}O_9$ (HRMS), was obtained as colourless needles. Comparison of the ^{1}H NMR and ^{13}C NMR data of **4** with those of weisiensin A (**7**) indicate that they have the same structural pattern except for the substituents on C-3 and C-11 [6]. In the ^{1}H NMR spectrum, the signal due to H-3 is shifted downfield from δ 3.72 in **7** to δ 5.07 in **4**, which suggests that an acetoxyl group is at the C-3 position in **4**. The EI mass spectral fragment ion peaks at *m/z* 252 ($C_{13}H_{16}O_5$) and 240 ($C_{13}H_{20}O_4$) resulting from the cleavage of B-ring (suggesting that two acetoxyl groups are in the A-ring) [7] support this assumption. The other difference between **4** and **7** is the upfield shift of C-11 from δ 69.3 in **7** to δ 66.6 in **4**, the downfield shifts of C-9 and C-12 from δ 55.5 and 38.6 in the latter to δ 59.2 and 41.4 in the former. Acetylation of **4** with acetic anhydride in pyridine in the usual manner affords the monoacetate **8** as the sole product. The hydroxyl group at C-11 in **4** is acetylated as shown by the downfield shift of δ 5.07 to 6.06. The ^{13}C NMR spectrum of **8** is identical to that of weisiensin A diacetate [6]. Therefore, the structure of **4** can be represented as *ent*-6β,11α-dihydroxy-1β,3α,7α-triacetoxykaur-16-en-15-one.

EXPERIMENTAL

General. Mps: uncorr; ^{1}H NMR: 300 MHz; ^{13}C NMR: 75 MHz. TMS as int. standard. EIMS: 70 eV.

Plant material. Rabdosia leucophylla (Dunn) Hara was collected in Kangding, Sichuan province of China in October, 1994. It was identified by Prof. Zhengyi Wu of Kunming Institute of Botany, Academia Sinica. The voucher specimen (SK-9402) is deposited in the Chengdu Institute of Biology, Academia Sinica.

Extraction and isolation. Dried and finely powdered aerial parts (6 kg) were extracted with EtOH for 14 days at room temp. and the solvent evapd. The residue was refluxed (×3) in MeOH–H_2O (9:1) and the extract decolourized with active charcoal. The transparent light-yellow filtrate was concd to *ca* 1.2 l and the deposit obtained on standing removed. The MeOH soln was concd and the residue dissolved in MeOH–H_2O (1:9) and shaken with EtOAc. The EtOAc soln was evapd *in vacuo* to yield 80 g of a yellow gum which was subjected to CC over silica gel (1.0 kg). The column was eluted with $CHCl_3$ and increasing proportions of Me_2CO–$CHCl_3$. All components were further purified by repeated CC on silica gel and recrystallization, yielding in order of increasing polarities: leucophyllin A (**1**) (1.5 g), B (**2**) (240 mg), C (**3**) (20 mg), D (**4**) (80 mg).

Leucophyllin A (**1**). Mp 287–289°. $[\alpha]_D^{12}$ −47.5° ($CHCl_3$; *c* 0.58); UV $\lambda^{CHCl_3}_{max}$ nm (log ε): 242 nm (5.41); IR ν^{KBr}_{max} (KBr) cm^{-1}: 3438, 1743, 1739, 1716, 1648, 1242, 1140, 1069, 989; EIMS *m/z*: 430 $[M\text{-}AcOH]^+$, 370 $[M\text{-}AcOH \times 2]^+$, 310 $[M\text{-}AcOH \times 3]^+$, 284, 231, 198, 149, 138; HRMS *m/z*: 490.2199 $[M]^+$, calcd for $C_{26}H_{34}O_9$: 490.2203. ^{1}H NMR (pyridine-d_5): δ 6.67 (1H, *d*, *J* = 5 Hz, 11α-H), 5.90, 5.18 (each 1H, *s*, 17-H_2), 5.16 (1H, *s*, 7α-H), 4.78 (1H, *t*, *J* = 3 Hz, 3α-H), 4.45 (1H, *dd*, *J* = 5, 11 Hz, 1β-H), 2.96 (1H, *s*, 9β-H), 2.91 (*br d*, *J* = 3 Hz, 13α-H), 2.23, 2.01 and 1.72 (each 3H, *s*, OAc × 3), 1.40, 1.31, 0.89 (each 3H, *s*, tert.Me × 3); ^{13}C NMR (pyridine-d_5): Table 1.

Acetylation of leucophyllin A (**1**). Acetylation of **1** (60 mg) with 2 ml Ac_2O–pyridine (1:1), at room temp. overnight gave **6** (62 mg) after work-up in the usual manner. ^{1}H NMR ($CDCl_3$): δ 5.87 and 5.26 (each 1H, *br s*, 17-H_2, 5.55 (1H, *d*, *J* = 4 Hz, 11α-H), 5.24 (1H, *dd*, overlapped, 1β-H), 4.87 (1H, *s*, 1α-H), 4.66 (1H, *t*, *J* = 3 Hz, 3α-H), 3.60 (1H, *s*, 5β-H), 3.08 (1H, *br d*, *J* = 3 Hz, 13α-H), 2.62 (1H, *s*, 9β-H), 2.28, 2.14, 2.05 and 1.86 (each 3H, *s*, OAc × 4), 1.38, 1.29, 0.80 (each 3H, *s*, tert.Me × 3); ^{13}C NMR ($CDCl_3$): δ 78.3 (C-1), 29.1 (C-2), 76.9 (C-3), 35.5 (C-4), 51.6 (C-5), 204.0 (C-6), 79.8 (C-7), 52.8 (C-8), 54.1 (C-9), 49.0 (C-10), 68.4 (C-11), 37.9 (C-12), 35.8 (C-13), 33.7 (C-14), 201.1 (C-15), 149.3 (C-16), 114.2 (C-17), 25.9 (C-18), 22.1 (C-19), 15.0 (C-20), 170.2, 170.0, 169.3, 169.0, 21.6, 21.3, 21.1 and 21.0 (OAc × 4).

Leucophyllin B (**2**). Mp 241–243°. $[\alpha]_D^{12}$ −36.3° (Me_2CO; *c* 0.40); UV $\lambda^{CHCl_3}_{max}$ nm (log ε.): 233 (5.28); IR ν^{KBr}_{max} cm^{-1}: 3480-3426, 1738, 1721, 1712, 1645, 1371, 1282, 1243; HRMS *m/z*: 448.2075 $[M]^+$, calcd for $C_{24}H_{32}O_8$ 448.2097; ^{1}H NMR (pyridine-d_5): δ 7.11 and 5.03 (each 1H, *br s*, disappeared after D_2O treatment, OH × 2), 5.93 and 5.21 (each 1H, *s*, 17-H_2), 5.66 (1H, *s*, 7β-H), 5.31 (1H, *d*, *J* = 5 Hz, 11α-H), 4.84 (1H, *t*, *J* = 3 Hz, 3α-H), 4.33 (1H, *t*, *J* = 8 Hz, 1β-H), 3.42 (1H, *s*, 5β-H), 3.01 (1H, *s*, 9β-H), 2.81 (1H, *br d*, *J* = 5 Hz, 13α-H), 2.20, 1.96 (each 3H, *s*, OAc × 2), 1.47, 1.30, 1.20 (each 3H, tert.Me × 3); ^{13}C NMR (pyridine-d_5): Table 1.

Acetylation of leucophyllin B (**2**). Acetylation of **2** (20 mg) with 2 ml Ac_2O–pyridine (1:1), at room temp. for 4 days gave a diacetate. The process was monitored by TLC. The diacetate had the same R_f value as **6** on TLC. Its ^{1}H NMR and ^{13}C NMR spectral data was identical to those of **6**.

Leucophyllin C (**3**). Mp 244–246°. $[\alpha]_D^{12}$ +27.4° (Me_2CO; *c* 0.19); IR ν^{KBr}_{max} cm^{-1}: 3400, 3342, 1740, 1705, 1240, 1080, 1040, 992; EIMS *m/z*: 390 $[M\text{-}AcOH]^+$, 330 $[M\text{-}AcOH \times 2]^+$, 312 $[M\text{-}AcOH \times 2\text{-}H_2O]^+$, 198, 138, 149, 121; HRMS *m/z*: 450.2222 $[M]^+$, calcd for $C_{24}H_{34}O_8$: 450.2254; ^{1}H NMR (pyridine-d_5): δ 6.69, 5.04 and 5.04 (each 1H, *br s*, disappeared after D_2O treatment, OH × 3), 5.64 (1H, *m*, 11α-H), 5.37, 5.16 (each 1H, *br s*, 17-H_2), 5.25 (1H, *s*, 7α-H), 4.85 (1H, *t*, *J* = 3 Hz, 3α-H), 4.62 (1H, *m*, 15α-H), 4.56 (1H, *dd*, *J* = 5, 11 Hz, 1β-H), 3.68 (1H, *br s*, 5-H) 3.21 (1H, *br s*, 9-H), 2.63 (1H, *br d*, *J* = 3 Hz, 13-H), 2.24 and 1.95 (each 3H, *s*, OAc × 2), 1.43, 1.41, 1.09 (each 3H, *s*, tert.Me × 3); ^{13}C NMR (pyridine-d_5): Table 1.

X-Ray structure determination. A unique diffractometer data set (ω scan mode, $2\theta_{max}50°$, monochromatic MoK_α radiation (λ = 0.71073 Å) was measured at ≈ 294 K yielding 2706 reflections; of these 2630 were independent reflections (R_{int} = 0.0214) and used in the full matrix least squares refinement without absorption correction. All of the coordinate parameters and anisotropic thermal parameters for C, O atoms and all of the coordinate parameters, isotropic thermal parameters for hydrogen atoms were refined. Conventional residuals on F^2 at convergence were $R = 0.039$, $wR^2 = 0.076$. All data were measured on a Simens P4 Four-Circl diffractometer system powered at 50 kV 30 mA with XSCANS program package. SHELXL 86 program was used to solve the structure, and SHELXL 93 to refine it. Neutral atom scattering factors were employed. The molecular structure is depicted in Fig. 1, the chirality being assigned by the chemistry. The atomic coordinates bond lengths, bond angles, thermal parameters and structure factors are available at the Cambridge Crystallographic Centre.

Crystal data: $C_{24}H_{34}O_8$, M_r 450.51. Orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 7.972(1)$, $b = 11.762(1)$, $c = 24.866(4)$ Å, $V = 2331.6(6)$ Å^3, $D_c = 1.283$ g cm^{-3}, $Z = 4$; F (000) = 968, $\mu = 0.096$ mm^{-1}; specimen dimension 0.38 × 0.34 × 0.26 mm.

Leucophyllin D (**4**). Mp 231–233°. $[\alpha]_D^{12} + 2.3°$ (Me_2CO; c 0.51); UV λ_{max} ($CHCl_3$) nm (log ε): 240 (5.20); IR ν_{max}^{KBr} cm^{-1}: 3600-3300, 1736, 1725, 1712, 1642, 1264, 1244, 1060; EIMS m/z: 432 [M-AcOH]$^+$, 279, 241, 149, 121; HRMS m/z: 492.2360 [M]$^+$, calcd for $C_{26}H_{36}O_9$: 492.2368; ^1H NMR (pyridine-d_5): δ 7.07 (1H, *d*, $J = 4$ Hz, 6α-OH), 5.87 and 5.15 (each 1H, *br s*, 17-H_2), 5.53 (1H, *d*, $J = 4$ Hz, 7α-H), 5.35 (1H, *t*, $J = 8$ Hz, 1β-H), 5.07 (1H, overlapped, 11α-H), 4.88 (1H, *br s*, 3α-H), 4.33 (1H, *m*, 6β-H), 2.23, 2.04 and 1.99 (each 3H, *s*, OAc × 3), 1.90, 1.51 and 0.98 (each 3H, *s*, tert.Me × 3); ^{13}C NMR (pyridine-d_5): Table 1.

Acetylation of leucophyllin D (**4**). Acetylation of **2** (20 mg) with 2 ml Ac_2O–pyridine (1:1) at room temp. for 5 days gave **9** (21 mg) $C_{28}H_{38}O_{10}$ needles. ^1H NMR (pyridine-d_5): δ 6.06 (1H, *d*, $J = 4$ Hz, 11α-H), 5.92, 5.20 (each 1H, *br s*, 17-H_2), 5.56 (1H, *d*, $J = 3$ Hz, 7α-H), 5.48 (1H, *t*, $J = 9$ Hz, 1β-H), 4.94 (1H, *br s*, 3α-H), 4.37 (1H, *m*, 6β-H), 2.31, 2.27, 2.02 and 1.90 (each 3H, *s*, OAc × 4), 1.72, 1.53 and 1.00 (each 3H, *s*, tert.Me × 3); ^{13}C NMR (pyridine-d_5): δ 80.4 (C-1), 28.2 (C-2), 78.8 (C-3), 37.3 (C-4), 42.9 (C-5), 70.1 (C-6), 75.3 (C-7), 48.8 (C-8), 55.2 (C-9), 43.1 (C-10), 68.6 (C-11), 38.7 (C-12), 36.8 (C-13), 36.6 (C-14), 205.6 (C-15), 150.8 (C-16), 112.2 (C-17), 29.9 (C-18), 23.8 (C-19), 15.7 (C-20), 21.7, 21.4, 21.1, 20.8, 170.4, 170.2, 170.2 and 169.3 (OAc × 4).

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